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Basic Tin(II) Sulphates

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Of the various basic tin(II) sulphates reported in the literature, the only one preparable as a clearly defined crystalline phase from aqueous solution is tritin(II) oxide dihydroxide sulphate, $Sn_3(OH)_2OSO_4$. The pure material can be obtained from solutions of pH 1·5—2·4 but precipitates obtained from solutions above pH 2·4 are not true basic salt phases. The dehydration of tritin(II) oxide dihydroxide sulphate at 230° and the subsequent decomposition of the product, tritin(II) dioxide sulphate, are discussed.

THE first precipitate obtained on addition of an alkali or alkali carbonate solution to a solution of a tin(II) material is either a complex or a basic salt phase. A complex is obtained when the solution contains species such as phosphite [1] or acetate [2] that are stronger donors towards tin(II) than the hydroxide ion, and precipitation of the complex generally begins at pH 4—6. In the absence of a strong donor, the product is a basic salt and precipitation begins in more acid solutions (pH 1—2).

Tobias [3] has studied the hydrolysis of tin(II) compounds by potentiometric measurements and shown that the basic ions in solution, before precipitation, are $SnOH^+$, $Sn_2(OH)_2^{2+}$, and the polynuclear ion $Sn_3(OH)_4^{2+}$, which predominates. This work was confirmed by others [4] who used Tobias's experimental data in a recalculation of the stability constants of the hydroxide–tin(II) cations. Evidence was found in the later calculations for the additional species $Sn_2(OH)_3^+$. Any basic salt phases obtained from solutions of tin(II) materials by precipitation should be derivatives of the predominant tetrahydroxotritin(II) ion or of a closely related species.

Only two basic tin(II) salt systems, nitrate and chloride, have been studied in detail. The crystalline basic tin(II) nitrate,[5] $Sn_3(OH)_4(NO_3)_2$, is a derivative of the $Sn_3(OH)_4^{2+}$ ion and is the only distinct phase precipitated from tin(II)–nitrate solutions. A recent careful study [6] of the basic tin(II) chloride has shown that only one distinct basic salt phase, tetratin(II) hexahydroxide dichloride, is precipitated. Ion-exchange studies on saturated tin(II) chloride solutions just before precipitation of the basic salt provided some evidence for the presence of the ion $Sn_3(OH)_4^{2+}$. We now report a similar study of the basic tin(II) sulphate system.

The precipitation of basic tin(II) sulphates has been reported by a number of workers. There is, however, little agreement on the formulae of the materials obtained. Their preparation was first described by

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[1] J. D. Donaldson, W. Moser, and W. B. Simpson, *J. Chem. Soc.*, 1964, 323.

[2] J. D. Donaldson and J. F. Knifton, *J. Chem. Soc. (A)*, 1966, 332.

[3] R. S. Tobias, *Acta Chem. Scand.*, 1958, **12**, 198.

[4] Chia-Chang Liang and Ya-Ming Tu, *Zhur. neorg. Khim.*, 1964, **9**, 1334.

[5] J. D. Donaldson and W. Moser, *J. Chem. Soc.*, 1961, 1996.

[6] J. D. Donaldson and W. Moser, *J. Chem. Soc.*, 1963, 1727.

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Berthelot [7] and Longi [8] and later by Ditte [9] who reported the existence of the three materials $5SnO,SnSO_4,H_2O$, $2SnO,SnSO_4,3H_2O$, and $4SnO,2SnSO_4,3H_2O$. Carson,[10] however, stated that only two distinct phases were obtained, *viz.*, $SnO,SnSO_4$ and $2SnO,SnSO_4,nH_2O$. The only other known basic tin(II) sulphate is Sn_2OSO_4 but this material has been prepared [11] by hydrothermal techniques, not by precipitation.

The variation with pH, in the composition of the material precipitated under nitrogen from a de-æreated solution of tin(II) sulphate on addition of de-æreated solution of 2N-sodium hydroxide was studied by chemical analysis and *X*-ray diffraction powder photography. The results (Table 1) show that only two distinct phases can be identified in the precipitates, *viz.*, a basic sulphate phase and hydrous tin(II)oxide. The first precipitate obtained on addition of the alkali solution is the crystalline basic salt, $Sn_3O(OH)_2SO_4$, and the pH remains constant at about 2 while most of the tin(II) is precipitated at this phase.

TABLE 1

Variation in composition with pH of product for the basic tin(II) sulphate system

pH	Tin(II) (%)	Total tin (%)	Sulphate (%)	Water (%)	Phases identified by *X*-ray powder diffraction
1·54	70·7	70·8	19·3	3·5	Basic sulphate
2·00	70·7	70·7	19·2	3·2	
2·32	70·8	70·8	19·2	3·5	
2·65	73·1	73·1	15·1	3·5	
3·20	75·4	75·5	12·5	3·7	Some lines of basic sulphate and hydrous oxide
3·80	76·3	76·5	12·2	3·7	
4·00	76·7	77·0	10·9	3·8	
4·70	79·0	80·4	4·56	4·6	
5·30	78·8	82·0	3·77	4·7	
7·10	80·8	82·1	1·62	4·8	
10·70	80·1	82·4	1·40	4·9	Hydrous oxide *
11·20	79·6	82·1	Traces	5·0	

* Ref. 12.

All precipitates obtained from solutions of pH 1·5—2·7 have the same composition and *X*-ray powder pattern. Above pH 3·2, however, the analytical composition of the precipitates varies considerably with pH and the *X*-ray diffraction powder lines due to the basic sulphate are superseded and ultimately replaced by lines due to hydrous tin(II) oxide. The various basic salt compositions reported previously merely represent the composition, as found by analysis, of heterogeneous stages in the replacement of sulphate by hydroxide.

The mean analytical results on three samples of the basic sulphate (Table 2*a*) confirm the composition $2SnO,SnSO_4,H_2O$ for the material. Since oxide ions cannot co-exist in a solid structure with free water, the analytically determined water must be present as hydroxide and the most satisfactory formula for the basic ion in the material would be $Sn_3O(OH)_2^{2+}$. This ion could be formed from the predominant basic species, $Sn_3(OH)_4^{2+}$, by loss of one molecule of water. This is in agreement with a previous suggestion [3] that the tetrahydroxotritin(II) ion might lose water as precipitation of a basic salt occurred.

The thermal stability of tritin(II) oxide dihydroxide sulphate was studied in a melting-point apparatus, in a vacuum grid, and by differential thermal analysis. The basic tin(II) sulphate loses water in one stage at 230° and the initial decomposition product is a yellow oxysulphate, $Sn_3O_2SO_4$. The mean analytical data for three samples are given in Table 2*b*. The Mössbauer spectrum of tritin(II) dioxide sulphate prepared at 230° shows a small peak owing to the presence of tin(IV) oxide. As the temperature is increased the colour of the material gradually darkens and the intensity of the tin(IV) Mössbauer peak increases. This increase in stannic oxide content was confirmed by chemical analysis. At 405° the $Sn_3O_2SO_4$ decomposes with a slight explosion to yield predominantly tin(IV) oxide (*X*-ray diffraction data) and sulphur dioxide (infrared characterisation). Small quantities of tin were also identified by Mössbauer spectroscopy. The differential thermal analysis curves for basic tin(II) sulphate and for tin(II) sulphate are shown in the Figure. The thermal decomposition of tin(II) sulphate to tin(IV) oxide and sulphur dioxide at 387° is known to be stoicheiometric [13] and is represented by the drop in the differential thermal analysis curve that begins at about 390°. The decomposition is complete before the exothermic peak at 502° and we suggest that this feature represents the crystallisation of tin(IV) oxide after its initial formation as an amorphous material. The differential thermal analysis curve for tritin(II) oxide dihydroxide sulphate has four features: (1) an endothermic peak at 236° which represents the decomposition to tritin(II) dioxide sulphate, (2) a second irreversible endothermic peak at 289°, (3) an exothermic peak at 405° due to the explosive decomposition of tritin(II) dioxide sulphate, and (4) a peak at 482° that is similar to the exothermic peak in tin(II) sulphate and which we again attribute to the crystallisation of tin(IV) oxide. The endothermic peak at 289° cannot be due to the formation of a high-temperature modification

TABLE 2

Analytical data for the basic tin(II) sulphates

(*a*) Crystalline precipitated phase

	(i)	(ii)	(iii)	Reqd. for $2SnO,SnSO_4,H_2O$
Tin(II) (%) ...	70·8	70·7	70·8	70·9
Total tin (%)	70·8	70·9	70·9	
Sulphate (%)	19·4	19·3	19·2	19·1
Water (%) ...	3·5	3·3	3·4	3·6

(*b*) Decomposition product at 230°

	(i)	(ii)	(iii)	Reqd. for $2SnO,SnSO_4$
Tin(II) (%) ...	73·2	73·3	73·4	73·6
Total tin (%)	73·8	73·8	73·7	
Sulphate (%)	20·0	20·1	20·3	19·9
Water (%) ...	0	0	0	0

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[7] A. B. Berthelot, *Mem. d'Arcueill*, 1807, **161**, 1.

[8] A. Longi, *L'Orosi*, 1885, 235.

[9] A. Ditte, *Ann. Chim. Phys.*, 1882, **27**, 159.

[10] C. M. Carson, *J. Amer. Chem. Soc.*, 1926, **48**, 906.

[11] G. Wernfors, *Acta Chem. Scand.*, 1961, **15**, 1007.

[12] J. D. Donaldson and W. Moser, *J. Chem. Soc.*, 1961, 835.

[13] J. D. Donaldson and W. Moser, *J. Chem. Soc.*, 1960, 4000.

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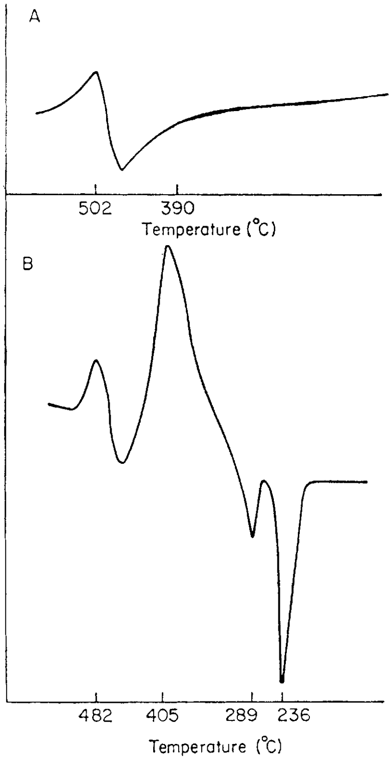
because it is an irreversible feature. Moreover, samples taken just before and after the peak gave identical X-ray diffraction powder and Mössbauer data, except for an increase in the amount of tin(IV) oxide present after 290°. We therefore attribute the weak endothermic peak at 289° to the oxidation of some of the tin(II) present to tin(IV). A similar oxidation of tin(II) to tin(IV) is known in aqueous hydrous tin(II) oxide systems.[12]



Differential thermal analysis curves for (A) tin(II) sulphate and (B) basic tin(II) sulphate

Crystallography.—(a) *Tritin*(II) *oxide dihydroxide sulphate*. Acicular crystals which show parallel extinction and low birefringence. Crystal data: $Sn_3O(OH)_2SO_4$, $M = 502{\cdot}2$, orthorhombic, $a = 4{\cdot}97 \pm 0{\cdot}005$, $b = 13{\cdot}15 \pm 0{\cdot}01$, $c = 12{\cdot}21 \pm 0{\cdot}01$ Å, $U = 798$ Å^3, $D_m = 4{\cdot}12$ (by loss of weight in benzene), $Z = 4$, $D_c = 4{\cdot}18$. Space-group $Pbcm$ (D_{2h}^{11}, No. 57), or $Pca2_1$ (C_{2v}^{5}, No. 29). Cu-K_α-radiation, single-crystal rotation and Weissenberg photographs about a and b axes.

(b) *Tritin*(II) *dioxide sulphate*. Crystal data: $Sn_3O_2SO_4$, $M = 484{\cdot}2$, orthorhombic, $a = 5{\cdot}02 \pm 0{\cdot}01$, $b = 13{\cdot}80 \pm 0{\cdot}02$, $c = 15{\cdot}43 \pm 0{\cdot}02$ Å, $U = 1069$ Å^3, $D_m = 4{\cdot}48$ (by loss of weight in benzene), $Z = 6$, $D_c = 4{\cdot}51$. Cu-K_α-radiation. Cell dimensions were obtained from X-ray powder data because no suitable single crystal could be obtained.

Table 3 contains the X-ray diffraction powder data for tritin(II) oxide dihydroxide sulphate and Table 4 the data for tritin(II) dioxide sulphate. For the basic tin(II) sulphate the spacings have been indexed by comparison of single-crystal and powder photographs and by calculation from the unit-cell dimensions.

TABLE 3

X-Ray powder data for tritin(II) oxide dihydroxide sulphate

d (Å)	Relative intensity	Index of reflection	$d_{calc.}$	d (Å)	Relative intensity	Index of reflection	$d_{calc.}$
6·11	m	002	6·11	2·00	mw	160	2·00
5·79	ms	021	5·79	1·977	vw	161	1·979
4·96	vw	100	4·96	1·961	m	045	1·961
4·65	vw	110	4·65			135	
4·46	vw	022	4·48	1·932	w	063	1·930
4·36	vw	111	4·34	1·912	w	233	1·909
3·97	ms	120	3·96	1·888	ms	242	1·886
3·86	w	102	3·85	1·812	ms	126	1·811
3·78	ms	121	3·77	1·734	ms	046	1·731
3·70	w	112	3·70			252	1·732
3·45	vvw	023	3·46	1·677	m	164	1·677
3·33	vvs	122	3·33	1·632	m	065	1·632
3·15	vvw	131	3·17	1·598	mw	302	1·598
3·17	s	041	3·17	1·560	vvw	180	1·561
3·05	vs	004	3·05	1·543	m	137	1·542
2·89	vs	042	2·90	1·528	mw	008	1·527
2·84	m	123	2·84	1·513	w	182	1·513
2·67	mw	141	2·67	1·473	w	147	1·472
2·56	m	043	2·56	1·454	m	255	1·452
2·50	w	142	2·50			272	1·456
2·45	vw	210	2·44			304	1·456
2·42	m	124	2·42	1·427	m	175	1·427
2·29	m	025	2·29	1·392	vw	351	1·393
		151	2·28	1·366	mw	352	1·366
		221		1·316	w	0100	1·316
2·24	vw	044	2·24	1·301	vw	208	1·301
		134		1·282	vw	086	1·280
2·19	vw	060	2·19	1·264	vw	1101	1·265
2·16	vvw	115	2·16	1·255	vw	257	1·255
		230		1·238	vw	186	1·238
2·13	vw	231	2·13	1·219	vvw	0010	1·221
2·09	vvw	213	2·09			420	
2·08	vvw	125	2·08				
2·04	vvw	006	2·04				

TABLE 4

X-Ray powder data for tritin(II) dioxide sulphate

d (Å)	Relative intensity	Index of reflection	$d_{calc.}$	d (Å)	Relative intensity	Index of reflection	$d_{calc.}$
7·71	ms	002	7·71	2·01	vvw	224	2·01
6·95	ms	020	6·90	1·927	vvw	008	1·928
6·17	vvw	021	6·30	1·878	w	056	1·881
4·66	mw	110	4·71	1·850	m	028	1·857
3·86	m	004	3·86	1·792	vvw	235	1·793
3·45	vw	040	3·45	1·759	mw	156	1·761
3·33	vvw	024	3·37	1·690	m	260	1·696
3·29	vw	131	3·31	1·541	w	0010	1·542
3·21	s	123	3·19	1·493	w	247	1·493
3·01	mw	015	3·01	1·460	vw	191	1·460
2·92	ms	034	2·96	1·384	vvw	0100	1·380
2·86	ms	043	2·86	1·339	vvw	0311	1·341
2·80	m	124	2·80			258	1·338
2·73	vvw	051	2·72	1·269	vvw	277	1·268
2·61	ms	052	2·60			293	1·268
2·50	vvw	200	2·51	1·243	vvw	382	1·243
2·44	vw	211	2·44			347	1·243
2·35	mw	220	2·35	1·221	vvw	197	1·221
2·26	vvw	116	2·26	1·207	vvw	431	1·207
2·23	vvw	213	2·23	1·117	vvw	1121	1·118
2·12	mw	232	2·12	1·101	vvw	460	1·102
2·07	vvw	224	2·07				

EXPERIMENTAL

Preparation of the Basic Tin(II) *Sulphate Phase in a Pure Crystalline Form*.—Because of the ease of oxidation of bivalent tin, all stages of the preparation were carried out under oxygen-free nitrogen. Stannous sulphate[13] (20 g.)

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was dissolved in water (80 ml.) and a 2N-ammonia solution was added until a permanent precipitate was obtained; the solution was heated and further alkali added until crystals began to deposit on the sides of the vessel. The solution was cooled and the crystalline product filtered off, washed with water, alcohol, and ether, and dried by suction and *in vacuo* over potassium hydroxide pellets.

The basic tin(II) sulphate obtained is a crystalline solid which is insoluble in, and unattacked by, water or organic solvents. It is soluble in dilute mineral acids and alkali. On storage the crystals are stable for at least twelve months.

Analysis.—We determined stannous and total tin by Donaldson and Moser's [14] method, and sulphate gravimetrically as barium sulphate. Water was determined by heating the sample in a flow of oxygen and collecting the water in an anhydrone absorbtion tube.

Differential Thermal Analysis.—The materials were heated in a Gallenkamp temperature-controlled furnace at the rate of 10°/min. The fluctuations in e.m.f. caused by phase changes were detected by thermocouples and plotted on a Rikadenki Kogyo recorder. In all studies the reference substance was alumina.

Mössbauer Spectroscopy.—The Mössbauer apparatus has been described previously.[15]

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